Will Zigzag Graphene Nanoribbon Turn to Half Metal under Electric Field?

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Abstract

At B3LYP level of theory, we predict that the half-metallicity in zigzag edge graphene nanoribbon (ZGNR) can be realized when an external electric field is applied across the ribbon. The critical electric field to induce the half-metallicity decreases with the increase of the ribbon width. Both the spin polarization and half-metallicity are removed when the edge state electrons fully transferred from one side to the other under very strong electric field. The electric field range under which ZGNR remain half-metallic increases with the ribbon width. Our study demonstrates a rich field-induced spin polarization behavior, which may leads to some important applications in spinstronics.

Since its isolation by mechanical exfoliation[1], graphene, a single graphite layer, has attracted a broad research interest. Because of its high carrier mobility and huge coherence distance at room temperature[2,3] it has been expected to be a very promising candidate of the future electronics materials. Along this direction, graphene nanoribbon (GNR), which is a graphite layer terminated in one direction with a specific width, were synthesized[2,3,4]. It is now well known that zigzag edge GNRs (ZGNRs) are semiconductors with two localized electronic edge states[5,6,7,8]. These two states are ferromagnetically ordered, and they antiferromagnetically coupled each other.

The spin degree of freedom of ZGNRs is very important considering their possible application in spintronics[9,10], where it is essential to realize electron transport through only one spin channel. With one metallic spin component and another semiconducting or insulating spin channel, half metal is an ideal material for spintronics. Based on density functional theory (DFT) calculations with the local density approximation (LDA), Son et al[11]. predicted that ZGNRs become half-metallic when an external transverse electric field is applied, which opens the possibility of the spintronics application for graphene.

Recently, Rudberg et al[12]. revisited the problem of the ZGNR electronic structure under electric field. They argued that although ZGNRs are spin-selective semiconductor, they never show half-metallicity if nonlocal exchange interaction is considered by using B3LYP functional. However, their study is limited to a specific ZGNR with 8 zigzag chains (8-ZGNR) and of finite length. Therefore, it is still an open question if ZGNR will turn to half metal under electric field.

In this letter,to clarify this issue, we report a careful study on the electronic structures of n-ZGNRs (n=5, 6, 7, 8, 9, 10, 12, and 14) with B3LYP functional. In our model, n-ZGNR is flat in x-y plan, with n zigzag chains along y direction. The edges of ZGNRs are saturated by hydrogen atoms. Periodic boundary condition (PBC) is used to consider ZGNRs with infinite length, just as shown in Fig. 1. Our calculations were carried out with the CRYSTAL03 package[13], which utilizes atom-centered Gaussian basis sets[14]. All-electron basis sets were adopted for both C[15] and H.[16] A reciprocal space sampling was made on a Monkhorst-Pack grid with a shrinking factor sufficient to converge the total energy to within eV per unit cell. A modified Broyden scheme[17], following the method proposed by Johnson[18], was applied in the SCF iteration.

We first consider the 8-ZGNR studied by Rudberg et al[12]. As shown in Fig. 2 (a), without

electric field, the energy gaps for both spin channels are 1.23 eV, very close to the 1.34 eV for ribbon of length 7.1 nm[12]. With the increase of the external electric field, the spin-down band gap decreases rapidly, and becomes zero when the electric field strength reaches 0.65 V/Å. On the other hand, the spin-up channel remains semiconducting under all external electric fields. Therefore, B3LYP also predict the electric field induced half-metallicity for the infinite long 8-ZGNR. However, the critical electric field obtained here is much larger than previously predicted by LDA (about 0.2 V/Å)[11]. Another important new feature revealed by our calculation is that the half-metallicity will be destroyed by a too strong electric field. As shown in Fig. 2 (a), the metallic character in the spin-down channel disappears when the electric field reaches 0.8 V/Å, Therefore, the answer to the title question is yes, and 8-ZGNR will turn to half metal under a limited range of external electric fields.

To understand the electric field response of 8-ZGNR, we plot its spin densities (ρ_α(r)-ρ_β(r)) of 8-ZGNR in Fig. 2 (c). Without electric field, we obtained a spin density very similar to the previous results[11,12]. It distributes on all carbon atoms, and decays from the edges to the middle. Each spin-up and spin-down density is mainly distributed at one side of the ribbon. By applying a 0.3 V/Å external electric field, the spin density in the middle of the ribbon is reduced, but the two edges are only little affected. When the electric field increases further and the ribbon becomes half metal, the spin density at the two edges is greatly reduced, and there is almost no spin density on the middle part. Finally, when the field reaches 0.9 V/Å, the system becomes spin-unpolarized. Rudberg et al.[12] found the magnetization decrease with the increase of electric field too. However, in their limited length case, the spin density disappears first from the two ends of the ribbon, and some magic patterns formed along the y direction under some fields, which directly leads to the half-metallicity unavailable for ribbons of finite length.

As shown in Fig. 3 (a) and (b), the projected density of states (PDOS) of 8-ZGNR is obtained by projecting electronic bands to three parts: atomic orbitals at the left/right C atom chain (C-L/C-R), and other C atoms (C-M). As shown in Fig. 3 (a), without external electric field, the two edge states are degenerate and with opposite spin directions. The degeneration of the two edge states is removed when external electric field is applied, due to the different electrostatic potentials at the two sides. The energy difference between these two edge states changes with the electric field strengths. When the occupied manifest of the left edge state meets the unoccupied manifest of the right edge state, changer transfer

occurs and the spin-down channel becomes metallic. Under an electric field of 0.9 V/Å, all electrons of the right edge state have been transferred to the left edge, making the spin density quenched. Thus, the half-metallicity is closely related to the electron transfer from right to the left.

It is interesting to check whether electric field can reduce half-metallicity for other ribbons with different widths. As shown in Fig. 3 (c), our calculations predict that all n-ZGNRs (n=5, 6, 7, 9, 10, 12, and 14) can display half-metallic behavior under suitable external field. The critical electric field to achieve half-metallicity decreases with the increase of ribbon width. This can be easily understood by the different electric field requirements to generate the same electrostatic potential difference between the left and the right side of n-ZGNR[11]. As shown in Fig. 3 (d), n-ZGNR remains half-metallic only at a limited range of electric field. With the increase of the ribbon widths, the corresponding field range increases too. The reason is that it is easier for wider ZGNRs to induce bands crossing in the spin-down channel by electric field. Band crossing leads to charge transfer. Once the electron transfer removes the spin polarization, the half-mtallicity has already been destroyed.

In summary, we have performed hybrid functional calculations with PBC to study the electronic structures of ZGNRs under external electric field. We find that the nonlocal exchange interaction does not remove half-metallicity of ZGNRs, and the contrary prediction by Rudberg et al[12]. should be an effect of finite length. The half-metallic behaviors are correlated with the partial electron transfer between the two edges of the ribbons and the band crossing caused by the additive electric potential difference under the electric field. A full edge state electron transfer removes spin polarization, and thus also the half-metallicity. The electric field range at which ZGNR remains half-metallic increases with the ribbon width. This new prediction may lead to some important applications of ZGNR in spintronics, such as switches and sensors.

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FIG. 1: (Color online) The structures of zigzag graphene nanoribbons, green balls are C atoms, blue balls are H atoms. The rectangle drawn with solid lines denotes the unit cell, and the arrow line represents the direction of external electric fields.

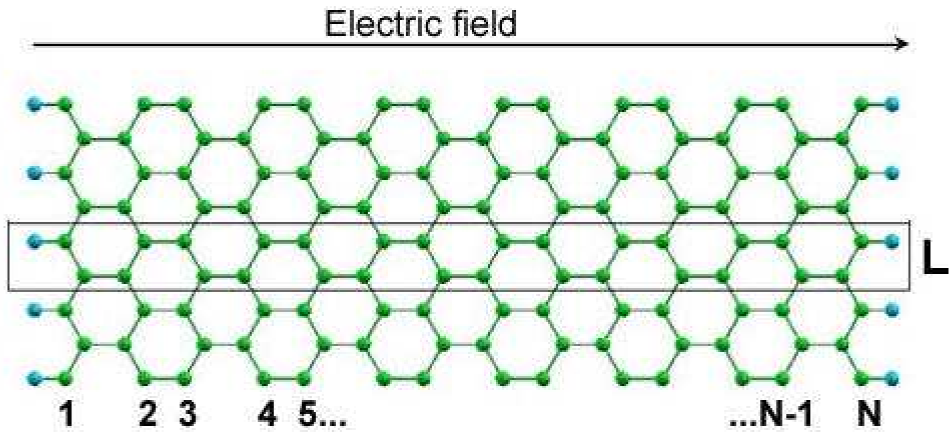

FIG. 2: (Color online) (a) Spin-up (blue) and spin-down (red) 8-ZGNR band gaps against external electric fields. (b) Spin-up (blue) and spin-down (red) 8-ZGNR band structure with E = 0.65 V/Å. (c) The spin densities of 8-ZGNR under different external electric fields, red for positive values and blue for negative.

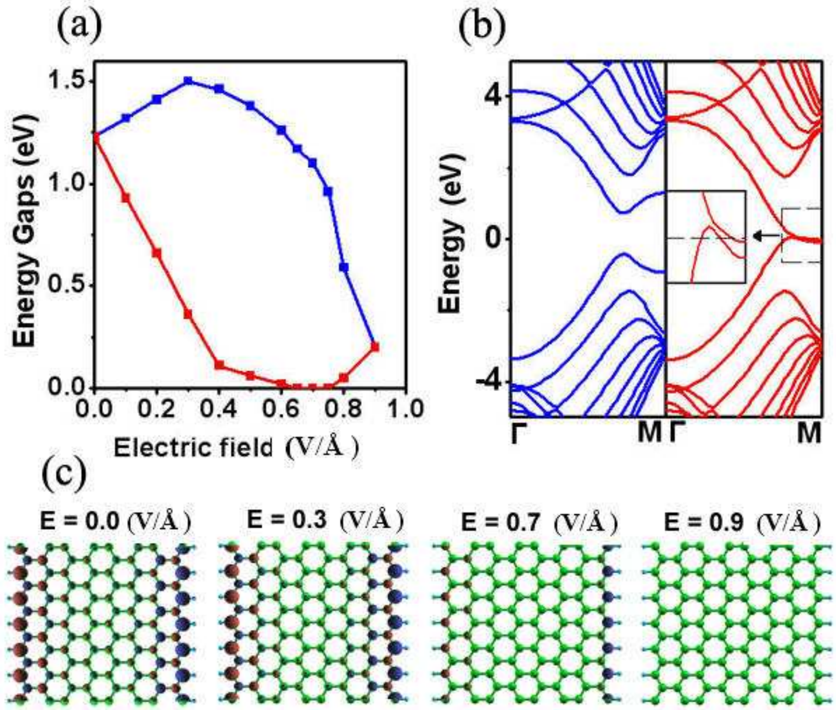

FIG. 3: (Color online) Project density of states (PDOS) of 8-ZGNR under external electric field of (a) 0.0 V/Å, (b) 0.9 V/Å, positive for spin-up, negative for spin-down. (c) N-ZGNR band gaps against external electric fields for n= 7, 9 , 10, 12, 14, the line with squares represents spin-up channel, and filled circles for spin-down one. (d) The critical electric fields (E_t) to achieve half-metallicity, and the range of electric fields strength (from E_t to E_t +ΔE) to keep half-metallicity for ribbons with n= 5, 6, 7, 8, 9, 10, 12, 14.